## U.S. Army Center for Health Promotion and Preventive Medicine



TOXICOLOGY STUDY NO. 87-XE-03N3-05
ASSESSING THE POTENTIAL ENVIRONMENTAL CONSEQUENCES
OF A NEW ENERGETIC MATERIAL: A PHASED APPROACH
SEPTEMBER 2005



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### 14. ABSTRACT

The U.S. Army Environmental Quality Technology Ordnance Environmental Program developed a protocol to address environmental, safety and occupational health (ESOH) risks during the research and development of new energetic materials. This work is being performed by a team led by the U.S. Army Center for Health Promotion and Preventive Medicine. The protocol established ESOH properties as critical performance parameters equivalent to traditional parameters such as energy, sensitivity, weight, yield and cost. This will enable researchers to determine and refine ESOH properties throughout development—through modeling and simulation in the early stages and testing in the later stages. Researchers will use this knowledge to identify and mitigate potential ESOH risks at each stage of development.

This protocol will reduce the risk of ESOH impacts from the fielding of new energetic materials. Researchers will address all materials with high ESOH risks as soon as they are identified. If unacceptable ESOH risks cannot be reduced, development of the material will be halted, or risks will be mitigated. This knowledge will help in preparing other required documents that assess ESOH impacts, including the Programmatic Environment, Safety and Occupational Health Evaluation and the Environmental Assessment.

### 15. SUBJECT TERMS

Environmental, Health, Energetics, USACHPPM, ESOH, Risk Assessment

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This effort is the result of a collaborative work group comprised of members of the Army research, development, test, and evaluation, health, and environmental communities to develop a hierarchical scheme for new energetic material evaluation. We thank Howard Beardsley for helpful reviews and comments. This initial plan has been reviewed by other environmental, safety and occupational health experts in the Army in cooperation with the acquisition community to determine the optimal method from which to move forward. This work is funded through the U.S. Army Environmental Quality Technology Ordnance Environmental Program through the Pollution Prevention Pillar.

### **Sponsor**

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Assessing the Potential Environmental Consequences of a
New Energetic Material: A Phased Approach

### **Data Requirement**

Not Applicable

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# EXECUTIVE SUMMARY TOXICOLOGY STUDY NO. 87-XE-03N3-05 ASSESSING THE POTENTIAL ENVIRONMENTAL CONSEQUENCES OF A NEW ENERGETIC MATERIAL: A PHASED APPROACH SEPTEMBER 2005

### 1. PURPOSE.

- a. Research, development, testing, training, and use of substances potentially less hazardous to human health and the environment is vital to the readiness of the U.S. Army. These activities involve the use of propellants, pyrotechnic, explosive, and incendiary compounds. Residues of these substances have been found in soil, air, and surface and ground-water samples; and over the life cycle of the components cost the military and the country billions of dollars. Safeguarding the health of Soldiers, civilians, and the environment requires an assessment of alternatives before they are fielded. Providing these assessments early in the research, development, test, and evaluation process can save significant time and effort if unacceptable risks are identified.
- b. The U.S. Army Environmental Quality Technology Ordnance Program is dedicated to finding replacements for substances causing environmental and/or occupational risks to health. As part of this program, each work unit is evaluated for environmental and occupational health. The purpose of this work unit is to find a less hazardous replacement for hydrazine in rocket propellant. Primary risks from hydrazine exposure include carcinogenic risks from the inhalation of vapors, particularly for Soldiers or workers.
- 2. CONCLUSIONS. This document provides the logic and rationale for assessing the toxicity and environmental compatibility of proposed new compounds for use in weapons and weapon platforms using a phased approach tuned to the relative investment made into each program. Initially, cost for obtaining relevant toxicological and environmental criteria necessary in evaluating the fate and transport of proposed new compounds is low, yet uncertainty is high. As the compounds and subsequent systems are refined, a greater degree of rigor in these data is proposed. Ultimately, it will result in a robust technical foundation for evaluating fate, transport, and effects for new weapons and platforms and provide for a more sustainable force.
- 3. RECOMMENDATIONS. It is recommended that the methods and logic presented herein serve as a guide and the data obtained from its use be considered as a data requirement for new weapon systems and platforms.

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## TOXICOLOGY STUDY NO. 87-XE-03N3-05 ASSESSING THE POTENTIAL ENVIRONMENTAL CONSEQUENCES OF A NEW ENERGETIC MATERIAL: A PHASED APPROACH SEPTEMBER 2005

- 1. REFERENCES. See Appendix A for a list of references used to prepare this report.
- 2. PURPOSE. This study is intended to provide the background and technical information that supports an integrated phased approach in the environmental evaluation of new energetic materials.
- 3. AUTHORITY. Military Interdepartmental Purchase Request (MIPR) #8ADATHR018, U.S. Army Research, Development and Engineering Command (RDECOM), (29 October 2007), (reference 1).

### 4. INTRODUCTION.

- a. Sustainable ranges are a vital component of defense readiness. Increasingly, energetic materials associated with range activities are being found in ground water, soils, and sediments. Risk assessment methods are used to determine if the levels of these substances are safe. This is the principle behind compliance and cleanup efforts that include the practice of industrial hygiene and many environmental standards such as ambient air quality standards, ambient water quality criteria, and others. The derivations of safe values are determined from an evaluation of controlled toxicity studies as well as other lines of evidence (e.g., epidemiological data) to determine what exposure conditions are safe. Exposure is estimated through sound demographic evaluations of human physiology and behavior. However, the concentration of any substance at the exposure point depends upon its persistence in the environment and its mobility (i.e., fate and transport). Analytical field data are often used in concert with environmental fate and transport models and specific exposure variables (e.g., amount of air breathed by an average adult during a given amount of time) to determine the degree of exposure.
- b. Adverse effects from environmental or occupational exposures as a result of the use of a new energetic material have the potential to significantly affect its development. Significant occupational risks to Soldiers may preclude its use. Life cycle costs associated with environmental risks can be substantial and need to be evaluated before new energetic materials are implemented in munitions and used. Lessons have been learned with previous use of energetic materials that were not screened during development. Examples include RDX, perchlorate compounds, and CL-20. Continued use of energetic materials not adequately evaluated may result in unacceptable operational and environmental health consequences, such as significant cleanup costs, closing of active ranges, and unacceptable limitations on range activities.

- c. Current U.S. Army regulations require that toxicity clearances be conducted for all substances that Soldiers may be exposed to as a result of a new program or system (reference 2). As part of the health hazard assessment process, described in Army Regulation (AR) 40-5, AR 40-10, Department of the Army Pamphlet (DA PAM) 70-3, and the Department of Defense (DOD) 5000 Deskbook, a chemical-specific toxicity clearance is required that addresses exposure to Soldiers as a direct result of use (references 3, 4, 5, and 6). The burden of collecting the necessary toxicity data is the responsibility of the proponent of the new system. As such, toxicity and exposure data are evaluated to address occupational safety and health concerns primarily; environmental health risks associated with the entire life cycle of an energetic material's use are evaluated to a limited extent.
- d. All new and modified energetic materials must be qualified before they can be implemented in weapons systems. The DOD Energetic Material Qualification Board (EMQB) requires that energetic materials undergo a series of rigorous qualification tests in accordance with several different standards, including MIL-STD-1751A and Naval Sea Systems Command Instruction 8020.5C (references 7 and 8), and various standardization agreements published by the North Atlantic Treaty Organization. Energetic materials are tested and qualified for a number of different characteristics, including but not limited to the following:
  - Stability characterization
  - Thermal characterization
  - Compatibility
  - Ignition temperature
  - Explosive response when ignited
  - Electrostatic, impact, friction and shock sensitivity
  - Chemical, physical and mechanical properties
  - Variation of properties with age
  - Toxicity
  - Performance properties
- e. A Programmatic Environment, Safety and Occupational Health Evaluation (PESHE) must also be conducted as part of the systems engineering process for all acquisition programs (reference 2). The PESHE is a living document that helps in the formulation of a comprehensive environment, safety and occupational health (ESOH) risk management strategy for system acquisition programs. The PESHE addresses environmental regulatory compliance, safety and health management, and hazardous materials and waste management. However, the PESHE requires a robust environmental data set from which to make useful recommendations. Moreover, environmental fate, transport and subsequent toxicity are not specifically addressed when significant data gaps exist. A PESHE is not required for acquisition programs until Milestone B (Figures 1 and 2), which occurs after technology development. Therefore, the PESHE is not used to make go/no-go program decisions early in the research, development, test,

and evaluation (RDTE) of energetic materials. This results in a significant void in the ESOH risk management process.

- f. A method and/or process are needed that integrates environmental health needs with those of the energetic materials RDTE community. Ultimately, the acquisition program manager is responsible for the complete life cycle costs associated with any new weapon system. Program managers and other decision makers need sound information to help them continuously assess the potential environmental impact of new energetic materials. This information can be provided through predictive modeling in the early stages of RDTE and through testing and data collection in the later stages. Many models currently used in RDTE can provide information regarding the likelihood for adverse environmental effects. These models can utilize similarities in chemical structure to predict parameters that are important in estimating fate and transport for an unknown material by comparing it to a similar material with known properties. Toxicity can be estimated through a comparison of active functional groups (i.e., similarity of chemical structures). A phased, iterative approach is needed that provides decision makers information regarding the health and environmental compatibility of new energetic materials.
- g. Figures 1 and 2 illustrate this concept. The approach in Figure 1 portrays the current paradigm of waiting until a system is fielded before examining the ESOH impacts. This approach has the potential to result in fines, litigation, cleanup costs, and range closure. Depending on impact severity and system attributes, a program could be sent back to any stage of RDTE in order to mitigate the ESOH impacts. The approach in Figure 2 is an ideal paradigm where ESOH risks are evaluated at every stage of RDTE, ensuring that there are minimal impacts when the system is fielded. In addition to avoiding the costs directly related to ESOH impacts, the approach in Figure 2 eliminates the costs of taking a large step backward in the RDTE process.

### 5. BACKGROUND.

- a. Standards and regulations exist under the Toxic Substances Control Act and the International Organisation for Economic Co-operation and Development for developing and producing new chemicals (references 9 and 10). However, these apply to high production volume chemicals only, which do not include most energetic materials. There is no DOD, Army, or other standard or regulation that specifically applies to the development of new energetic materials.
- b. Methods to evaluate fate and transport depend on the environmental media and the chemical/physical properties of the material. For example, compounds like ammonium perchlorate that are water soluble are likely to infiltrate ground water. In like manner, materials that are not water-soluble and do not have a high affinity to soil particles (e.g., RDX) which can

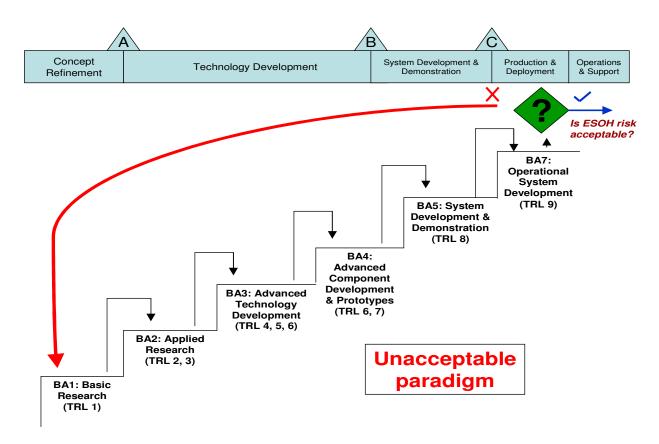
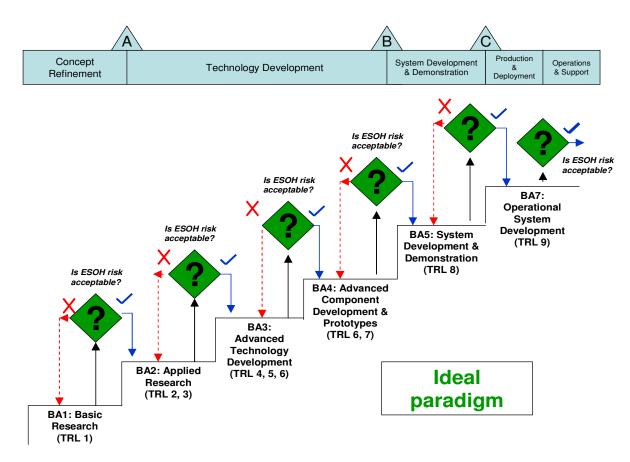


Figure 1. Unacceptable paradigm for the evaluation of new energetic materials throughout the RDTE process.



TRL = Technology Refinement Level

Figure 2. Ideal paradigm for the evaluation of new energetic materials throughout the RDTE process.

also migrate to ground water. Fate, transport, and toxicological properties can be estimated from models based on Quantitative Structural Activity or Property Relationships (QSARs/QSPRs) or can be measured in the laboratory. The former is relatively straightforward and inexpensive, but has a strong dependence on existing data for similar chemicals. In view of this, QSARs cannot be considered definitive and equivalent to experimental data. The latter is more reliable, but could require substantially more resources, including those associated with synthesis and testing.

c. Persistence is a parameter that can be difficult to estimate through computational or experimental means. Elements are persistent by definition; however, many compounds can be broken down by biologic and abiotic processes. These processes are dependant upon site-specific factors such as rainfall, temperature, and organic carbon content of the soil.

- d. Toxicity can be estimated by comparing chemical structures using a QSARs approach or can be measured from laboratory animal studies. Again, the latter method is much more reliable but requires much greater effort and associated cost. Toxicity to humans can be estimated from effects in laboratory mammal species (e.g., rats). Effects in other species such as birds and fish require materials to be tested in those species.
- e. Currently, there are no reliable alternatives to animal testing in the determination of toxicity. QSARs are only as reliable as the corroborating toxicological evidence and structural similarity of the substance under comparison. Sometimes, even small functional differences between similar energetic materials can lead to pronounced differences in toxicity (e.g., acute avian toxicity of dinitrotoluene compared with trinitrotoluene). Furthermore, some constituents may be relatively benign in certain ecological systems, but may result in significant environmental effects in other systems (e.g., toxicity to aquatic and terrestrial receptors may differ substantively).
- 6. SCOPE. The procedures suggested in this paper are intended to provide information to assist in the evaluation of environmental effects for new energetic materials during RDTE. These data can be integrated into existing frameworks (e.g., PESHE) and as such should provide more accurate, timely information for decision makers regarding the potential for adverse environmental consequences from complete life cycle use of new energetic materials.
- 7. APPROACH. A procedure is needed that balances sound environmental assessments of new energetic materials with the cost, schedule, and performance needs of the acquisition community. The primary mission of a program manager is to ensure that a system is functional and meets all performance requirements. It is therefore unreasonable to require the compilation and evaluation of a comprehensive set of environmental fate, transport, and effects data for a new energetic material before system and performance requirements have been met. Instead, potential environmental concerns can be evaluated and bounded using low-cost, low-effort methods in early stages of system development without constraining the decision makers. QSARs and similar models can provide fast, low-cost qualitative answers to environmental questions during basic RDTE to help decision authorities decide if it is wise to continue development. As a new energetic material proceeds through development, it may be necessary to refine environmental predictions by performing in vitro toxicity screening, limited animal testing, and experimental determination of chemical/physical property data. Based on each tier of information, decision makers can use these results as decision tools. This iterative approach (Figures 1 and 2) has the potential to save the DOD millions of dollars in acquisition, compliance, legal, and restoration costs and to sustain training on ranges and readiness of our forces. Figure 3 provides a summary of this hierarchical, iterative approach. Data developed during previous stages are used to build upon the data needs in subsequent stages.

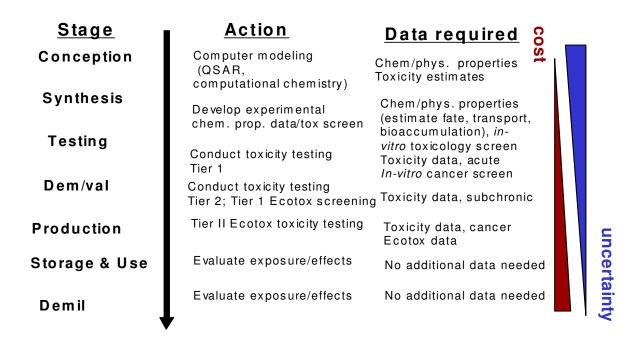


Figure 3. General hierarchical approach to the development of environmental data.

### a. Conception.

- (1) At this stage of energetic material development, molecular relationships and characteristics are examined to evaluate the properties of a new material. These include molecular and electronic structure, stability, thermal properties, and decomposition pathways (if necessary). Also at this stage, performance and sensitivity requirements are assessed. If the candidate is suitable for further consideration, performance in gun or warhead configurations will be modeled to provide information on emissions. The predicted molecular and electronic structural properties can also be used in QSAR or other approaches to determine chemical/physical properties relating to toxicity, fate, and transport. The properties that are useful in estimating the extent of fate and transport include the following:
  - Molecular weight
  - Water solubility
  - Henry's law coefficient
  - Vapor pressure
    - o Liquid-phase vapor pressure
    - o Solid-phase vapor pressure

- Affinity to organic carbon (log K<sub>oc</sub>)
- Lipid solubility (octanol/water coefficient; log K<sub>ow</sub>)
- Boiling point
- Melting point
- Ionization potential
- (2) QSAR approaches can also be used to estimate toxicological impact. Toxicity QSAR models can often predict many toxicity parameters without doing animal studies. These data are used to rank new energetic materials, not to quantitatively evaluate them. These methods provide a relatively fast, low-cost method for developing the minimum amount of environmental data necessary for an initial evaluation of environmental impacts. They can be used as a basis for go/no-go decisions regarding further development and can serve to focus further research.

### b. Synthesis and Small Scale Screening Tests.

- (1) Following the conceptualization of a new material, it must be synthesized. Once it is shown that small amounts of a new energetic material can be produced, small scale screening tests must be performed to establish performance characteristics and sensitivity. If the material is found to be acceptable from a performance perspective, risks from an environmental and occupational perspective can be more reliably determined through small scale tests using actual material. These methods can be used to develop data that can increase confidence in environmental fate, transport, and toxicity predictions. In addition, analytical chemistry methods are also needed at this stage. Analytical chemistry and standard experimental methods can be used to develop the following data:
  - Water solubility
  - Vapor pressure
  - Log K<sub>oc</sub>
  - Log K<sub>ow</sub>
  - Boiling point
- (2) Relative acute toxicity can be evaluated using relatively low cost *in vitro* cell culture techniques. Different concentrations of a new energetic material are evaluated alongside conventional energetic material using cell death and other endpoints. These dose-response curves can be used to ascertain relative toxicity and thus can be used for ranking purposes.
- c. <u>Demonstration Testing</u>. This stage involves testing new energetic materials in specific weapon system configurations. At this stage, greater masses of material are being synthesized but not yet at a production capacity. Since workers and Soldiers will be exposed at some level during testing, a greater investment in the program is required to proceed past this stage. More robust toxicity data are needed regarding environmental and occupational exposures. These data will be used to form the technical basis for toxicity clearances required in health hazard

assessments. At this stage, it is also cost effective to provide a more robust dataset regarding fate and transport mechanisms. Important parameters to develop at this stage include:

- Environmental ½ lives (soil, water, sediment; aerobic / anaerobic conditions; modeled approaches)
- Sorption (using triad approach; i.e., respective to clay, silica, and sand)
- Acute and subchronic toxicity (rodent bioassays)
- Identification of combustion and breakdown products
  - o Soil microbial breakdown evaluation
- Identification of the potential for bioaccumulation and/or biomagnification

### d. Production.

- (1) During production, specific energetic material formulations have been developed and mass production is planned. Small differences in material formulations may have a significant effect on fate, transport, and toxicity properties. Before a new energetic material is fielded and used in large quantities on ranges, the following environmental data are typically needed.
  - Environmental ½ lives (soil, water, sediment; aerobic / anaerobic conditions; experimental data, if needed).
  - Friability
  - Dissolution rate
  - Cancer *in vitro* screening assays (Note: If compounds show the propensity for cancer, animal testing may be necessary.)
  - Ecotoxicology information
    - o 96-hour or 7-day minnow studies
    - o Invertebrate assays (soil, water, sediment)
    - o Avian bioassay (acute, subchronic)
    - o Plant uptake models
- (2) These data should now be used in a quantitative risk assessment context to determine the degree of hazard. This assessment, including prospective future characterization of ranges, can be used to estimate range sustainability and to help bracket future potential liabilities. Integrated approaches involving state-of-the-art fate, transport, and hazard modeling can be accomplished using systems such as the Army Risk Assessment Modeling System (ARAMS). This approach provides specific information that decision makers can use to determine the degree of hazard. These data may also be integrated into the PESHE and the health hazard assessment to fully characterize the environmental risk posed by a new energetic material.

- (3) No further data are likely necessary in developing sustainment plans for subsequent stages (Storage and Use, Demilitarization); however, other data may be needed for alternate uses and purposes. It is advisable that experts in fate, transport, and toxicology review data at each acquisition stage to provide optimal professional judgments regarding alternatives.
- 8. COSTS AND PROJECTIONS. This proposal infers additional programmatic costs associated with energetic material RDTE and ordnance acquisition. The projected costs of these data requirements are estimated in Table 1.
- 9. IMPLEMENTATION. Recommendations will be implemented through a multi-step process to include the following actions.
  - Establish an Energetic Materials Environmental Working Group.
  - Draft a protocol for integrating the recommendations into energetic material RDTE.
  - Publish the protocol in a broad-based format, possibly as a commercial standard through the American Society for Testing and Materials.
  - Implement a military standard adopting the commercial standard, to be sponsored and managed by RDECOM.

### 10. CONCLUSIONS AND RECOMMENDATIONS.

a. Continued use of DOD ranges is a vital component to troop readiness and national security. The development and use of such a protocol provides decision makers with a phased, iterative approach to characterizing environmental risk that also balances cost and time constraints with performance requirements. This helps focus the RDTE of new energetic materials on the most promising candidates with the lowest associated environmental risk by identifying at an early stage any materials that exhibit the potential for negative environmental impacts. Although the procedures suggested herein increase the cost of developing new energetic materials, the cost is insignificant relative to those potentially incurred through remediation, range closure, litigation or late-stage failure of a program. It is therefore recommended that this process be integrated into ordnance programs as incremental requirements to help decision makers manage ESOH risk.

Table 1 Projected Costs

Stage	Data Requirement	Means	Estimated cost <sup>1</sup> (k=\$1000)	Timeline	
Conception	MW, water solubility, Henry's law, vapor pressure, K <sub>oc</sub> , K <sub>ow</sub> , boiling point, mammalian toxicity	QSAR/computational chemistry approaches	\$2k to \$5k	2 weeks	
Synthesis	Water solubility, K <sub>oc</sub> , K <sub>ow</sub> , vapor pressure, boiling point	Experimentally determined	\$15k	3 months	
Testing	Sorption Dissolution rate	Experimentally determined	\$15k	3 months	
	Environmental ½ lives (soil, water, sediment; aerobic/ anaerobic conditions)	Modeled approaches	\$3k to \$8k	1 month	
	Acute, subacute, subchronic toxicity testing	Experimentally determined	\$160k	5 months	
Production	Environmental ½ lives (soil, water, sediment; aerobic/ anaerobic conditions); Friability	Experimentally determined	\$15 to \$30k	3 months	
	Cancer <i>in-vitro</i> screening assays <sup>2</sup> Ecotoxicology	Experimentally determined Experimentally	\$7k to \$30k	3 months	
	information 96-hr minnow Invertebrate assay (soil,	determined	\$0.7k \$3k	4 weeks 2 months	
	water) Avian bioassay		\$150k	4 months	
	(acute, subchronic) Plant uptake models	Modeled data	\$2k to \$5k	3 weeks	
	-	Estimated Totals >	\$500k		

Notes:

<sup>1</sup> Cost based on best projection; does not include professional consultation.

<sup>2</sup> If compounds show the propensity for cancer, additional animal testing may be necessary.

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b. Finally, we recognize that a complete suite of rapid, accurate, predictive, and inexpensive
tests suggested by this report are lacking. This recommended approach is, however, a sound one
that would only benefit from improvements to the current state of the science. Therefore, we
recommend that deficiencies in such tests be promptly addressed and remedied.

MARK S. JOHNSON

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APPROVED:

MICHAEL A. MAJOR Program Manager

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